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METHOD FOR SAMPLING OF METHYL SALICYLATE VAPOR IN AIR USING PASSIVATED STAINLESS STEEL SYRINGES AND ANALYSIS BY GAS CHROMATOGRAPHY

by Amnon Birenzvige, Ph.D.
RESEARCH DIRECTORATE

Joseph P. Krasnec
SCIENTIFIC INSTRUMENTATION SPECIALISTS, INCORPORATED
Moscow, ID

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At the present time, the only available method for sampling organic vapor content in the air is a bubble collection followed by a gas chromatographic or spectroscopic analysis. This methodology, however, is limited to a medium-to-high vapor concentration range and medium-to-long sampling time. This report describes a study to extend the sampling range to short time periods (orders of few minutes).

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PREFACE

The work described in this report was authorized under Project No. 1C162706A553, CB Defense and General Investigation. This work was started in January 1986 and completed in April 1986.

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METHOD FOR SAMPLING OF METHYL SALICYLATE VAPOR IN AIR USING PASSIVATED STAINLESS STEEL SYRINGES AND ANALYSIS BY GAS CHROMATOGRAPHY

1. INTRODUCTION

In research relating to the behavior of chemical warfare agents on the battlefield, measurement of the concentration of organic vapors in the air is needed. Presently, the sampling and analysis of organic vapors is limited to bubblers with subsequent analysis (colorimetric, enzymatic, etc.). This Methodology is limited to medium-to-high vapor concentration levels and medium-to-long sampling periods. Expanding the sampling and analysis techniques and their applicable range of sampling period and concentration is needed. The table below lists possible sampling and analysis techniques and their applicable range of sampling periods and concentration for methyl salicylate (MeS) as a typical example. Efforts are underway at the U.S. Army Chemical Research, Development and Engineering Center (CRDEC) to develop sampling and analysis methodology for organic vapors using adsorbent tubes and gas chromatography (GC). This report describes a study to develop a sampling methodology for organic vapors using passivated stainless steel syringes followed by injection into a GC. MeS vapor was used in this work as a simulant for other organic vapors.

Sampling and Analysis Methods for MeS Vapors

Sampling Media	Analysis Method	Applicable Concentration Range	Applicable Sampling Period
Bubblers	Colorimetric Or GC	Medium To High	Medium To Long
Syringe	GC	Medium To High	Short
Adsorbent Tube	Thermal Desorption Followed By GC	Low To Medium	[illegible]
	Infrared	High	Continuous

2. EQUIPMENT AND MATERIAL

A Perkin-Elmer GC, model 900, was used for analysis of all samples. The GC was equipped with an OV-101 on Chromosorb W packed column (1/4 in. o.d., 10 ft long) and a Flame Ionization Detector (FID). Liquid MeS calibration mixtures (MeS in Hexane) were injected into the GC through a heated (250 °C) injector port with a glass syringe. The analysis was done isothermally at 200 °C and 50 ml/min carrier gas flow rate. Passivated stainless steel syringes were used for injecting the vapor samples into GC through a special six-port valve equipped with a fixed volume sample loop (0.1 ml and 5 ml, depending on MeS vapor concentration).* Known concentrations of MeS in air were prepared in passivated stainless steel grab samplers.

3. RESULTS AND DISCUSSIONS

The GC was calibrated with liquid mixtures of MeS in Hexane 1-1,000. Microvolume glass syringes were used for direct injection of the liquid samples onto the column via a heated injection port (250 °C). Following the liquid calibration, the GC was calibrated by using mixtures of MeS vapors in air. The vapor mixtures were prepared by injecting calculated volumes of MeS liquid into an evacuated, passivated stainless steel grab container and adding air until the desired concentration was reached. The gas mixtures were then injected into the GC via a six-port switching valve equipped with a 5-ml sample loop. A typical calibration curve is shown in Figure 1.

Examining the liquid and vapor phase chromatograms carefully, we noticed some tailing of the vapor phase MeS peak. Tailing of the vapor phase MeS peak indicates surface adsorption within the GC. The exposed surface area within the GC was small and did not affect the total amount recovered. This is confirmed by the fact that the MeS peak area in both cases remained unchanged.

Substantial loss of MeS vapor was observed when vapor samples were withdrawn from the stainless steel grab sampling containers with a stainless steel syringe and injected into the GC. In one test, a mixture of 10.3 ppm MeS in air was withdrawn with a syringe and injected into the GC (equivalent to 0.07 μg with a 5-ml sample loop). The first injection yielded only 34% of the original amount. Following the injection, the syringe was emptied, filled with zero air, and again injected into the GC. After four repeated

*During the passivation process, the surface free energy of the stainless steel was reduced by a proprietary electrochemical process due to formation of an Ni/Cr oxide layer on the surface. [Oliver, K.D., Pleil, J.D., and McClenny, W.A., "Sample Integrity of Trace Level Volatile Organic Compounds in Ambient Air Stored in Summa Polished Canisters," Atmospheric Environment Vol. 20, p 1403 (1986).]

injections, 94% of the MeS was recovered (see Figure 2). The MeS vapors absorb into the syringe surface; and after the intial injection, the vapors gradually desorb. Note that no surface losses were observed in the stainless steel grab containers because the surface-to-volume ratio for the containers is smaller than the ratio for the syringe - 0.26 versus 3.4, respectively, for a spherical canister of 6,000 ml and a syringe of 30 ml. In another test, a 67.7 ppm mixture was injected into the GC (equivalent to 0.46 μg with a 5-ml. sample loop). Only 0.22 μg were recovered (a loss of 52.5%). However, when the syringe was heated to 225 °C, over 90% of the MeS was recovered in the first injection. Repeated flushing of the syringe at elevated temperature increased the yield to over 99%.

Because of the surface adsorption phenomena, it is very important to ensure that the sampling syringe does not contain any residual MeS vapor from previous tests. Ensuring the sampling syringe does not contain any residual MeS vapors can be accomplished by heating the syringe to over 200 °C and injecting the syringe into the GC. The process should be repeated until no more MeS can be detected. Two injections are usually sufficient.

4. CONCLUSIONS AND RECOMMENDATIONS

Research indicates that MeS vapor concentration in ambient air can be monitored by collecting air samples in passivated stainless steal syringes with subsequent analysis by a GC equipped with an FID. Pronunced MeS adsorption at ambient temperatures is overcome by controlled thermal desorption before injecting the syringe contents into the GC. The sampling and analytical process is in fact the preferred method under conditions of relatively high MeS vapor concentration and low sampling time.

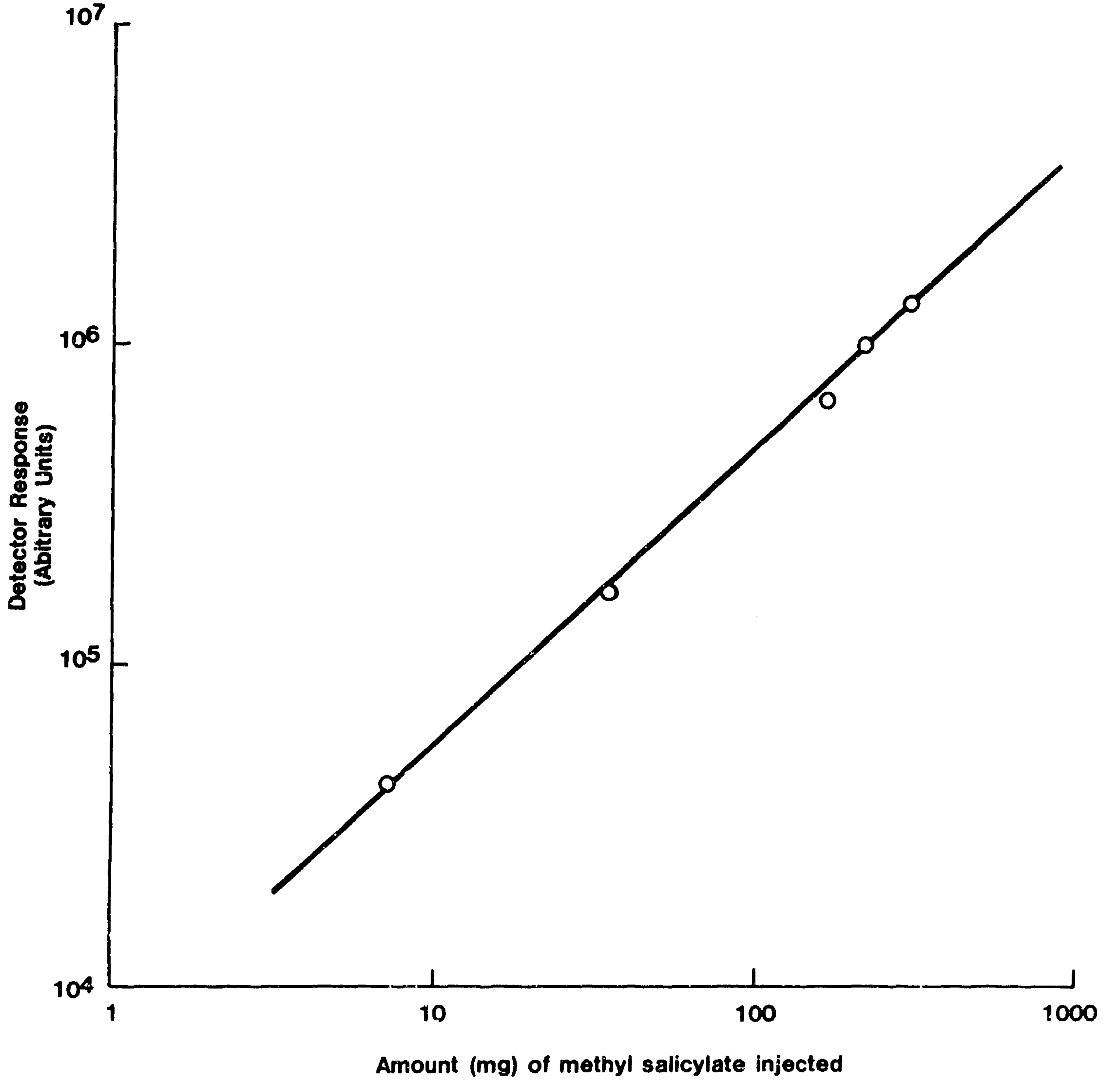

Figure 1. Calibration Of Methyl Salicylate By GC-FID

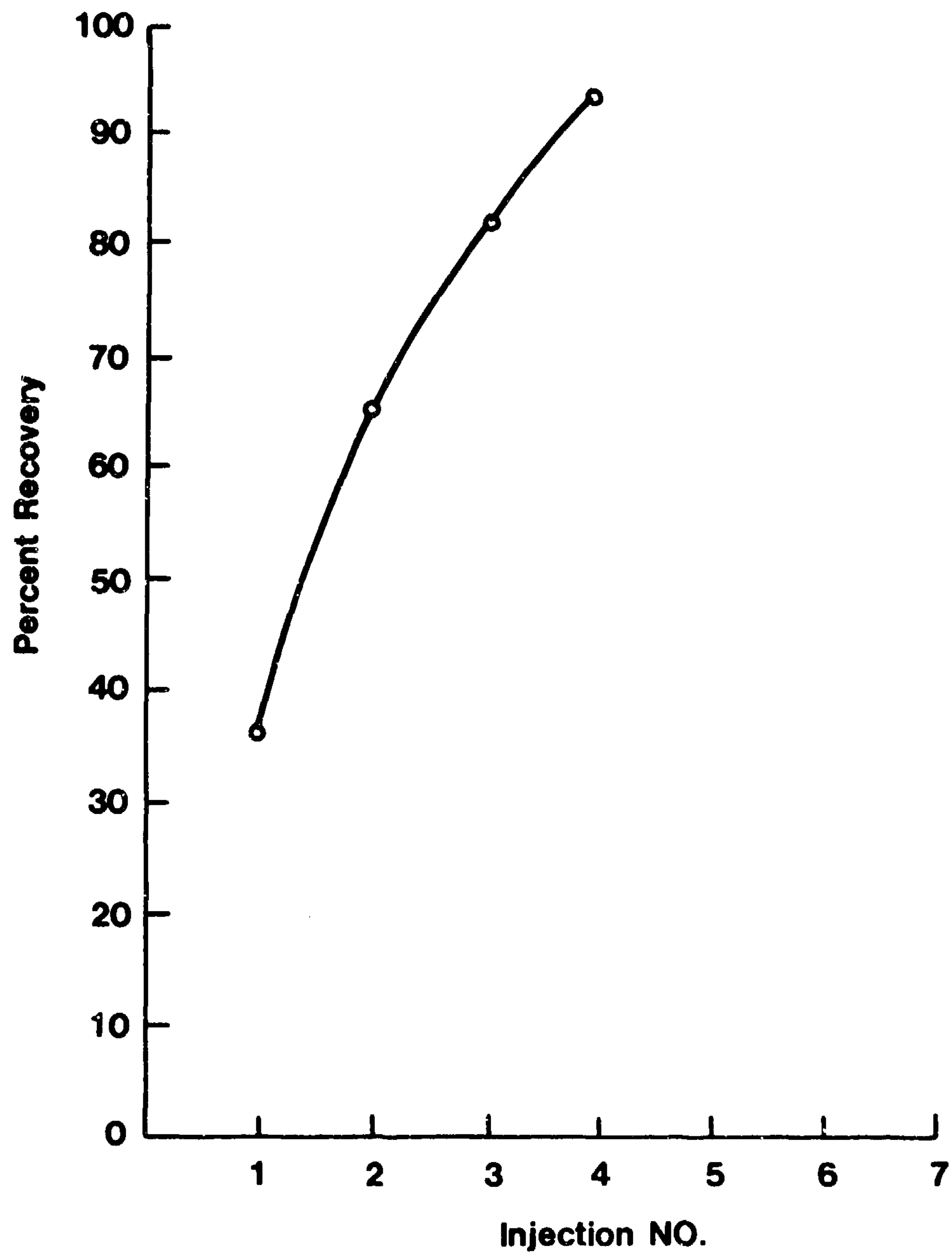

Figure 2. Percent Recovery Of Methyl Salicylate By Repeated Injections